

Integrated light in direct excitation and energy transfer luminescence

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Integrated light in direct excitation and energy transfer luminescence has been investigated. In the investigations reported here, monomolecular centers were taken into account. It was found that the integrated light is equal to the product of generation rate and time of duration of excitation pulse for both direct excitation and energy transfer luminescence.

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I. INTRODUCTION

Spectral and kinetic measurements are used to determine the characteristic features of the luminescence as well as the luminophors investigated. However, contrary to the spectral measurements, the kinetic measurements allows very often to give a quantitative description of the dependence investigated permitting the better determination of the mechanism of luminescence and, for example, electroluminescent device. Therefore, many papers are devoted to kinetic of luminescence^{1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29}

Some investigators have established correlated formulas to describe the time dependence of luminescence. For example, Chimczak *et al.* (1984, 1995) described theoretically very well time dependence of ZnS:Mn electroluminescence of thin film devices excited by short voltage pulse^{1,2}. The researches (1989) have also obtained good fitting of the electroluminescence to the experimental data during³ as well as after the end⁴ of rectangular exciting pulse. Berdowski *et al.* (1985) obtained very good description of emission of Tb³⁺ in CsCdBr₃ : Tb³⁺ upon excitation in ⁵D₃ level at 1.3 and 75 K⁵. Wang *et al.* (2003) have derived an analytical expression constructed as a sum of several products of Gauss function and exponential functions to describe the time dependence in ZnS:Er³⁺ thin films⁶. Kimpel *et al.* (1995) explained time behavior of the Cr²⁺ in ZnS⁷. Roura *et al.* have analyzed dynamics of the infrared photoluminescence in silicon powder⁸. All the cited above investigations allows obtaining integrated light of luminescence. However, up to now, nobody has described the integrated light, which is additional kind of investigations of luminescence kinetic. The aim of the paper is to describe the integrated light for direct excitation and energy transfer luminescence assuming monomolecular centers in the description.

II. DIRECT EXCITATION LUMINESCENCE

Let assume that monomolecular luminescent centers are excited by rectangular pulse. If direct excitation is the only process then the luminescence rises during the exciting pulse and begins to decay immediately after the

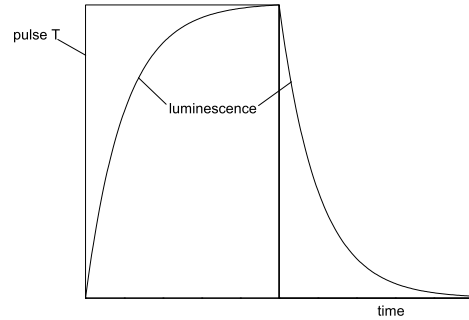


FIG. 1: Time dependence of direct excitation luminescence excited by rectangular pulse

end of the pulse (Fig. 1). For monomolecular centers we have

$$\frac{dn}{dt} = G - \alpha n, \quad (1)$$

where G is generation rate and n is number of excited luminescent centers at the time t . Resolving the equation we obtain

$$n = \frac{G}{\alpha}(1 - e^{-\alpha t}) + n_0 e^{-\alpha t}, \quad (2)$$

where n_0 is number of the excited centers at the end of the pulse. Taking into account that for monomolecular kinetic the luminescence intensity is $I = \alpha n$ and that lifetime τ is $1/\alpha$ we have

$$I = G(1 - e^{-t/\tau}) + I_0 e^{-t/\tau}, \quad (3)$$

where $I_0 = \alpha n_0$ is the luminescence intensity at the end of the pulse. If we assume that, at the start, the luminescent centers were not excited than the equation

$$I_d = G(1 - e^{-t/\tau}), \quad (4)$$

describes luminescence intensity during the exciting pulse and equation

$$I_a = I_0(1 - e^{-t/\tau}), \quad (5)$$

describes luminescence intensity after the end of the pulse. From the equation we can get formula used to determination of luminescence lifetime

$$\tau = \frac{t}{\ln(I_0/I)}. \quad (6)$$

Integrated light of direct excitation luminescence during the exciting pulse, obtained from equation (4), has form

$$S_d = \int_0^T I_d dt = GT + G\tau e^{-T/\tau} - G\tau. \quad (7)$$

After the end of the pulse the integrated light is described as

$$S_a = \int_0^\infty I_a dt = G\tau + G\tau e^{-T/\tau}. \quad (8)$$

Total integrated light of direct excitation luminescence is

$$S = S_d + S_a = GT. \quad (9)$$

III. ENERGY TRANSFER LUMINESCENCE

A. Luminescence excited by short pulse

In some cases, luminescence maximum appears after a time t_m (t_{m0} for very short pulse), considerably longer than the pulse duration T . Such behavior can be explained by assuming energy transfer between two monomolecular centers. The number of the transferring centers dn_1 which recombine during the time dt is

$$dn_1 = -\alpha_1 n_1 dt. \quad (10)$$

The change in the excited emitting centers is described as

$$dn_2 = dn_2' + dn_2'', \quad (11)$$

where $dn_2' = -dn_1$ and $dn_2'' = -\alpha_2 n_2 dt$. After mathematical treatments, the time dependence of the luminescence is given as

$$I = -\frac{dn_2''}{dt} = \frac{n_{01}}{\tau_2 - \tau_1} (e^{-t/\tau_2} - e^{-t/\tau_1}), \quad (12)$$

where n_{01} is the initial number of excited transferring centers and τ_1, τ_2 are the lifetimes of the transferring and emitting centers, respectively. The relation (12) is shown in Fig. 2. The curve in the figure attains its maximum at the time

$$t_{m0} = \frac{\tau_1 \tau_2}{\tau_2 - \tau_1} \ln \frac{\tau_2}{\tau_1}, \quad (13)$$

Both the last relations are in good agreement with experimental data for electroluminescence of thin film cells based on ZnS:Mn^{1,2}.

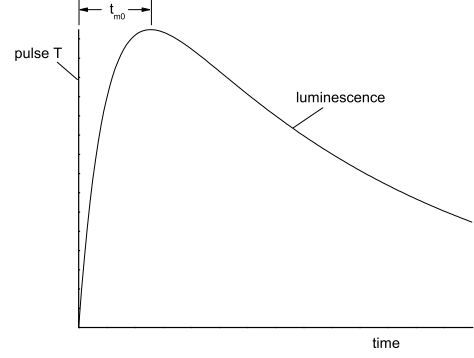


FIG. 2: Time dependence of energy transfer luminescence excited by short pulse

B. Time dependence of luminescence during rectangular exciting pulse

Let us assume, to explain the time dependence, that each part d of the exciting pulse T produces the elemental curve (12) (Fig. 3)³². After the short part d of the

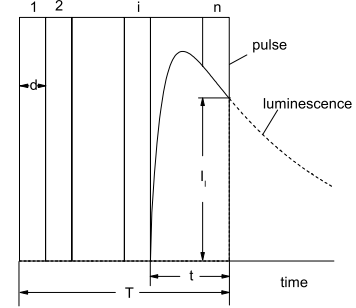


FIG. 3: Luminescence produced at the end of exciting pulse T by short parts d of the pulse

exciting pulse T , initial number of excited transferring centers is

$$n_{01} = Gd. \quad (14)$$

Intensity of the luminescence, at the end of the pulse T , produced by the part d_i is

$$I_i = \frac{Gd}{\tau_2 - \tau_1} (e^{-(n-i)d/\tau_2} - e^{-(n-i)d/\tau_1}). \quad (15)$$

At the end of the exciting pulse the luminescence intensity is

$$I = \sum_{i=1}^{n-1} I_i, \quad (16)$$

In order to calculate eq. (16) we will use

$$de^{-\frac{d}{\tau}} + de^{-\frac{2d}{\tau}} + \dots + de^{-\frac{(n-1)d}{\tau}} = d \frac{e^{-d/\tau}(e^{-(n-1)d/\tau} - 1)}{e^{-d/\tau} - 1}. \quad (17)$$

Taking into account that $T = nd$, we have

$$\lim_{d \rightarrow 0} \frac{e^{-T/\tau} - e^{-d/\tau} + de^{-d/\tau}/\tau}{-e^{-d/\tau}/\tau} = \tau(1 - e^{-\frac{T}{\tau}}). \quad (18)$$

On insertion of eq. (18) into eq. (16) the luminescence intensity at the end of the exciting pulse T is given by

$$I = \frac{G}{\tau_2 - \tau_1} \left(\tau_2(1 - e^{-T/\tau_2}) - \tau_1(1 - e^{-T/\tau_1}) \right). \quad (19)$$

If the relation (19) is assumed to be valid at any time $t \leq T$, the time dependence of the luminescence, during the exciting pulse T , is described as

$$I = \frac{G}{\tau_2 - \tau_1} \left(\tau_2(1 - e^{-t/\tau_2}) - \tau_1(1 - e^{-t/\tau_1}) \right). \quad (20)$$

This function, contrary to direct excitation luminescence, has got a point of inflection. This point appears at the same time t_{m0} , at which the first elemental luminescence curve (Fig. 3) excited by the first part d of the pulse T attains its maximum. The luminescence strongly increases with time until the time t_{m0} , when it tends to saturate. Equation (20) very well describes the electroluminescence of ZnS:Mn thin films³. Figures 4, 5 and 6 show relative

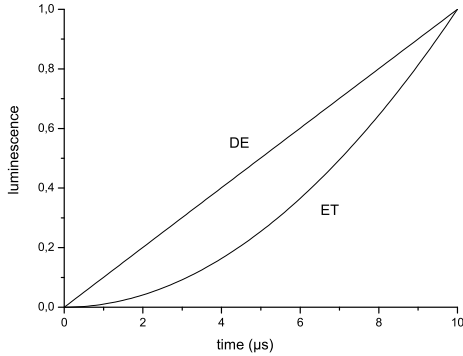


FIG. 4: Time dependence of luminescence during exciting rectangular pulse of 10 μs . DE - direct excitation, ET - energy transfer

comparison of both, direct excitation (DE) and energy transfer (ET), mechanisms. The curves in these figures were plotted at $\tau_1 = 100\mu s$ and $\tau_2 = 1000\mu s$. When the luminescence is excited by very short pulse of 10 μs (Fig. 4), then the luminescence at the first stage of excitation is practically not seen. In the case, as is seen in the figure, there is great difference between both mechanisms. For a longer width of the exciting pulse (Fig. 5

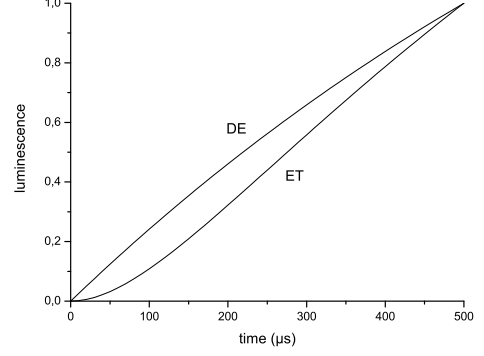


FIG. 5: Time dependence of luminescence during exciting rectangular pulse of 500 μs . DE - direct excitation, ET - energy transfer

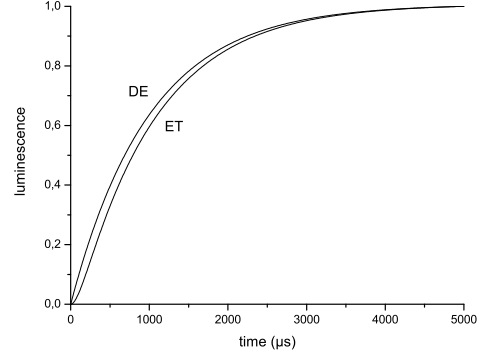


FIG. 6: Time dependence of luminescence during exciting rectangular pulse of 5000 μs . DE - direct excitation, ET - energy transfer

and 6), the difference in time dependence of both mechanisms disappears. Also, the difference disappears when the lifetime, τ_1 , of the transferring centre decreases. The small difference between both mechanisms in the case of great width of the exciting pulse or short lifetime of the transferring centre are probably the reason why experimental dependences similar to that of Fig. 6 are sometimes faulty assumed to be due to direct excitation. Integrated light of energy transfer luminescence during the rectangular exciting pulse, obtained from equation (20), has form

$$S_d = GT - \frac{G\tau_2^2}{\tau_2 - \tau_1} (1 - e^{-\frac{T}{\tau_2}}) + \frac{G\tau_1^2}{\tau_2 - \tau_1} (1 - e^{-\frac{T}{\tau_1}}). \quad (21)$$

C. Time dependence of luminescence after the end of rectangular exciting pulse

Similar to that of Sect. B, we assume that the exciting pulse consists of n short pulses d (Fig. 7)³³. The

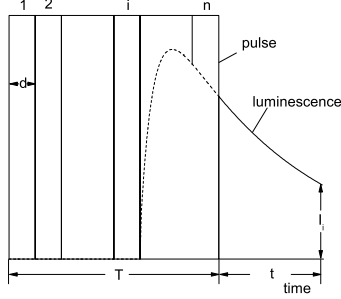


FIG. 7: Luminescence produced at the time t after exciting pulse T by short parts d of the pulse

luminescence produced by part d_i of the pulse T is

$$I_i = \frac{Gd}{\tau_2 - \tau_1} \left(e^{-\frac{t+(n-i)d}{\tau_2}} - e^{-\frac{t+(n-i)d}{\tau_1}} \right). \quad (22)$$

Using the same procedure, we have got the relation describing the time dependence of luminescence after the end of the exciting pulse, for energy transfer between two monomolecular centers as

$$I = \frac{G}{\tau_2 - \tau_1} \left(\tau_2 (1 - e^{-\frac{T}{\tau_2}}) e^{-\frac{t}{\tau_2}} - \tau_1 (1 - e^{-\frac{T}{\tau_1}}) e^{-\frac{t}{\tau_1}} \right). \quad (23)$$

Figure 8 shows the time dependence described by the

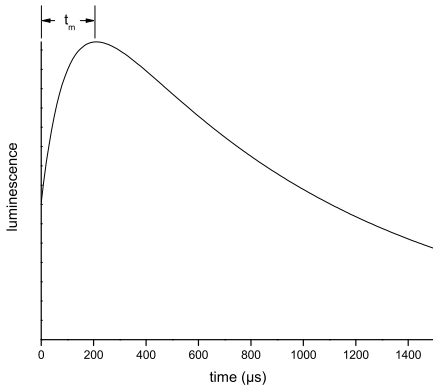


FIG. 8: Time dependence of energy transfer luminescence after exciting rectangular pulse

equation (23). For short exciting pulses, the luminescence intensity at the maximum, after the end of the exciting pulse, considerably exceeds the value of the luminescence intensity at the end of the pulse. The difference is smaller for longer pulse-duration and practically absent for very long pulses. However, even in the last case, the luminescence attains its maximum, after the end of the exciting pulse, at a time

$$t_m = \frac{\tau_1 \tau_2}{\tau_2 - \tau_1} \ln \frac{e^{-T/\tau_1} - 1}{e^{-T/\tau_2} - 1}. \quad (24)$$

As is seen, the time t_m depends on T . When T is going to 0, t_m is going to t_{m0} and the luminescence curve is going to that described by (12). When T is going to infinity, t_m is going to 0 and the time dependence is going to that described by (5). Contrary to direct excitation, the luminescence after the end of the exciting pulse (23) also depends on T . The equation (23) explains why the first experimental points, after the end of the exciting pulse, lie below straight line when time dependence of luminescence is plotted in semilogarithmic scale. From the (23), we obtain the integrated light of energy transfer luminescence after the end of the rectangular exciting pulse

$$S_a = \frac{G\tau_2^2}{\tau_2 - \tau_1} (1 - e^{-\frac{T}{\tau_2}}) - \frac{G\tau_1^2}{\tau_2 - \tau_1} (1 - e^{-\frac{T}{\tau_1}}). \quad (25)$$

Total integrated light of energy transfer luminescence is

$$S = GT. \quad (26)$$

IV. CONCLUSION

Time dependence of luminescence during and after a rectangular exciting pulse was discussed. In the case of direct excitation of luminescence, the intensity of the luminescence increases during the exciting pulse and begins to decay immediately after the end of the pulse. When there is energy transfer to luminescence center from another center then the luminescence can increase in intensity after the end of the excitation pulse before subsequently decaying. During the exciting pulse the luminescence is practically not seen at the first stage of excitation. The luminescence curve has got a point of inflection at the time t_{m0} (13). The energy transfer luminescence attains its maximum after the end of the exciting pulse at the time t_m (24). In the case of very short exciting pulses, there is a great difference between both mechanisms. For a long width of exciting pulse or very short lifetime of the transferring center, the difference disappears. It is the reason why it is sometimes faulty assumed that, for longer pulse lengths, the dominant excitation mechanism is direct excitation. It is shown in the paper, that total integrated light is proportional to the pulse length for direct excitation as well as energy transfer luminescence. From the experiment, it exhibits

that, for short exciting pulses, the integrated light is not proportional to the excitation pulse length^{24,34}. There is some excess in the region of short pulses. The results obtained in the paper show that the excess is not due to energy transfer mechanism.

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- ¹ E. Chimczak, W. S. Gordon, and M. Bertrandt-Żytkowiak, *Phys. Stat. Sol. (a)* **82**, 527 (1984).
 - ² M. Bertrandt-Żytkowiak and E. Chimczak, *Thin Solid Films* **256**, 136 (1995).
 - ³ E. Chimczak and M. Bertrandt-Żytkowiak, *Phys. Stat. Sol. (a)* **115**, 581 (1989).
 - ⁴ E. Chimczak and M. Bertrandt-Żytkowiak, *Acta Phys. Pol. A* **77**, 399 (1989).
 - ⁵ P. A. M. Berdowski, M. J. J. Lammers, and G. Blasse, *J. Chem. Phys.* **83**, 476 (1985).
 - ⁶ Y.-J. Wang, C.-X. Wu, M.-Z. Chen, and M.-C. Huang, *J. Appl. Phys.* **93**, 9625 (2003).
 - ⁷ B. M. Kimpel, K. Lobe, H. J. Schulz, and E. Zeitler, *Meas. Sci. Technol.* **6**, 1383 (1995).
 - ⁸ P. Roura, J. Costa, G. Sardin, J. R. Morante, and E. Bertran, *Phys. Rev. B* **50**, 18124 (1994).
 - ⁹ R. N. Bhargava, D. Gallagher, X. Hong, and A. Nurmikko, *Phys. Rev. Lett.* **72**, 416 (1994).
 - ¹⁰ A. N. Krasnov and P. G. Hofstra, *Prog. Crystal Growth and Charact.* **42**, 65 (2001).
 - ¹¹ G. C. John and V. A. Singh, *Phys. Rev. B* **54**, 4416 (1996).
 - ¹² C. Barthou, J. Benoit, P. Benalloul, and A. Morell, *J. Electrochem. Soc.* **141**, 524 (1994).
 - ¹³ Y. Zhang, M. D. Sturge, K. Kash, B. P. van der Gaag, A. S. Gozdz, L. T. Florez, and J. P. Harbison, *Phys. Rev. B* **51**, 13303 (1995).
 - ¹⁴ W. Busse, H. E. Gumlich, B. Meissner, and D. Theis, *J. Lumin.* **12-13**, 693 (1976).
 - ¹⁵ S.-Y. Seo, M.-J. Kim, and J. H. Shin, *Appl. Phys. Lett.* **83**, 2778 (2003).
 - ¹⁶ H. Weman, C. J. Harris, J. P. Bergman, M. S. Miller, J. C. Yi, and J. L. Merz, *Superlatt. and Microstruct.* **17**, 61 (1995).
 - ¹⁷ N. Harukawa, S. Murakami, S. Tamon, S. Ijuin, A. Ohmori, K. Abe, and T. Shigenari, *J. Lumin.* **87-89**, 1231 (2000).
 - ¹⁸ M. F. Joubert, B. Jacquier, C. Linarès, J. P. Chaminade, and B. M. Wanklyn, *J. Lumin.* **37**, 239 (1987).
 - ¹⁹ M. C. de Lucas, F. Rodrigez, and M. Moreno, *Phys. Stat. Sol. (b)* **184**, 247 (1994).
 - ²⁰ A. Wolfert, E. W. J. L. Oomen, and G. Blasse, *J. Sol. Stat. Chem* **59**, 280 (1985).
 - ²¹ P. A. M. Berdowski, J. van Herk, and G. Blasse, *J. Lumin.* **34**, 9 (1985).
 - ²² A. B. Suchocki, G. D. Gilliland, C. Powell, M. Bowen, and J. C. Walling, *J. Lumin.* **37**, 29 (1987).
 - ²³ T. C. Leslie and J. W. Allen, *Phys. Stat. Sol. (a)* **65**, 545 (1981).
 - ²⁴ E. Chimczak and J. W. Allen, *J. Phys. D: Appl. Phys.* **18**, 951 (1985).
 - ²⁵ Y. Zhang, M. D. Sturge, K. Kash, B. P. van der Gaag, A. S. Gozdz, L. T. Florez, and J. P. Harbison, *Superlatt. and Microstruct.* **17**, 201 (1995).
 - ²⁶ P. Bergman and B. Monemar, *J. Lumin.* **38**, 87 (1987).
 - ²⁷ C. D. Lee, H. L. Park, C. H. Chung, and S. K. Chang, *Phys. Rev. B* **45**, 4491 (1992).
 - ²⁸ M. O. Ramirez, D. Jaque, L. E. Bausá, I. R. Martín, F. Lahoz, E. Cavalli, A. Speghini, and M. Bettinelli, *J. Appl. Phys.* **97**, 093510 (2005).
 - ²⁹ H. Aizawa, M. Sekiguchi, T. Katsumata, S. Komuro, and T. Morikawa, *Rev. Sci. Instr.* **77**, 044902 (2006).
 - ³⁰ M. Kapoor, V. A. Singh, and G. K. Johri, *Phys. Rev. B* **61**, 1941 (2000).
 - ³¹ K. Thilsing-Hansen, M. T. Neves-Petersen, S. B. Petersen, R. Neuendorf, K. Al-Shamery, and H. G. Rubahn, *Phys. Rev. B* **72**, 115213 (2005).
 - ³² E. Chimczak, *J. Lumin.* **39**, 247 (1988).
 - ³³ E. Chimczak, *Z. Phys. B - Condensed Matter* **72**, 211 (1988).
 - ³⁴ N. E. Rigby and J. W. Allen, *J. Lumin.* **42**, 143 (1988).